

Chapter 6

Data Quality



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Data quality indicators (DQI) have been formulated to gauge the achievement of CASTNet quality objectives. DQI are quantitative and qualitative descriptors used in interpreting the degree of acceptability and utility of the data collected. The application of the DQI to the hourly, weekly, and annual data ensures that the data provided are of known and documented quality. An analysis of DQI goals based on 2001 measurements and a review of historical results indicate that CASTNet has produced and continues to produce data of the highest quality.

CASTNet was designed to fulfill the following objectives:

- To monitor the status and trends in regional air quality and atmospheric deposition;
- To provide information on the dry deposition component of total acid deposition, rural ground-level O₃ concentrations, and other forms of atmospheric pollutants that enter the environment as particles and gases;
- To assess and report on geographic patterns and long-term, temporal trends in ambient air pollution and acid deposition.

Consequently, the primary component of CASTNet is the measurement of sulfur and nitrogen species and cations at rural, regionally representative sites across the United States. These primary measurements are supplemented by measurements of meteorological conditions and ozone concentrations. DQI have been formulated to gauge the achievement of CASTNet objectives. DQI are

quantitative and qualitative descriptors used in interpreting the degree of acceptability and utility of the data collected. The DQI for CASTNet include precision, accuracy, completeness, representativeness, and comparability (Harding ESE, 2002c). In the following sections, precision of field measurements of pollutant concentrations on filters, laboratory precision and accuracy, precision of measurements of O₃ concentrations, and completeness of direct and calculated/aggregated measurements are presented. Historical statistics are also presented for comparison and to provide an overall indication of data quality over the history of the network. In addition to the information presented in this chapter, Harding ESE is preparing a 2001 QA Report. This report will detail the DQI measurement results and will include historical comparisons. Internal and independent audit results will be summarized.

Precision of Filter Concentrations

DQI and associated measurement criteria are listed in Table 6-1. These criteria are provided in terms of precision and accuracy of filter concentration data. The precision criteria apply to pairs of concentration data collected at collocated sampling systems and also to laboratory in-run replicate data. During 2001, collocated sampling systems were operated at ASH135/235, MCK131/231, and ROM206/406. The collocated sampling at MCK131/231 operated throughout the year. In July 2001, the collocated sampling was terminated at ASH235 and a collocated system was established at ROM206. The two sites at Rocky Mountain National Park are operated independently. ROM206 is operated on behalf of EPA and ROM406 on behalf of NPS. Historically, collocated systems have been operated at eleven sites.

In Figure 6-1, bar charts present precision statistics in terms of mean absolute relative percent difference (MARPD) both for the historical database (i.e., 1990 through 2000) and the 2001 data for ASH135/235, MCK131/231, and ROM206/406. Trace cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) are excluded from this analysis and are discussed later. The historical results vary from about 5 percent for particulate SO_4^{2-} to about 12 percent for particulate NO_3^- . The historical MARPD statistics for SO_4^{2-} and NH_4^+ met the criteria in Table 6-1. The results for SO_2 and HNO_3 were above the 5 percent criterion but were considered reasonable. The results for NO_3^- were significantly above the 5 percent goal. Historically, the precision of the particulate NO_3^- measurements has been consistently

worse than for the other analytes, possibly because nitrate concentrations were the lowest of all the pollutants.

The 2001 precision results indicate that three of the analytes measured at Ashland were above the historical results and two were below. The results from Mackville were all below the historical results. The precision data from the newly collocated sampling systems at Rocky Mountain National Park were comparable to the historical results, with the exception of the somewhat higher MARPD values reported for the two sulfur species.

The analytical precision results for five analytes and the three filter types for 2001 are presented in Figure 6-2. These results were based on analysis of 5 percent of the samples in each batch that were randomly selected for replication. The results of the analysis of the in-run replicates were compared to the results of original concentrations. The laboratory precision data met the 5 percent DQI goal (Table 6-1).

Precision statistics for 2001 for trace cations, based on both collocated ambient concentrations and laboratory in-run replicates, are summarized in Figure 6-3. The criterion is 10 percent. The MARPD data for ambient K^+ , Mg^{2+} , and Ca^{2+} were acceptable for Ashland and Mackville. The results for ambient Mg^{2+} at Rocky Mountain National Park were acceptable. The precision data for collocated K^+ and Ca^{2+} measurements at ROM206/406 exceeded the criterion.

Estimates of precision by analyte are based on collocated filter samples collected at ten sites over the history of the network. Historical precision statistics vary between 5 and 12 percent. Precision estimates for SO_4^{2-} and NH_4^+ met the DQI measurement criteria; the estimates for SO_2 and HNO_3 were considered acceptable. The precision of particulate NO_3^- measurements was above the DQI goal. The results for 2001 were comparable to historical results. Laboratory precision, which was estimated from in-run replicates, met all DQI objectives.

Table 6-1. Data Quality Indicators for CASTNet Laboratory Measurements*

Analyte	Medium	Method	Precision (MARPD)**	Accuracy (%)	Nominal Detection Limits
Ammonium (NH ₄ ⁺)	F	Automated colorimetry	10	90 - 110	0.02 mg-N/L
Sodium (Na ⁺)	F	ICAP-AE	10	90 - 110	0.005 mg/L
Potassium (K ⁺)	F	ICAP-AE	10	90 - 110	0.005 mg/L
Magnesium (Mg ²⁺)	F	ICAP-AE	10	90 - 110	0.003 mg/L
Calcium (Ca ²⁺)	F	ICAP-AE	10	90 - 110	0.003 mg/L
Nitrate (NO ₃ ⁻)	F	Ion chromatography	5	95 - 105	0.008 mg-N/L
Sulfate (SO ₄ ²⁻)	F	Ion chromatography	5	95 - 105	0.04 mg/L
Elemental Carbon	QF	TOA	10	90 - 110	0.04 µg -C/m ³
Organic Carbon	QF	TOA	10	90 - 110	0.10 µg -C/m ³
Total Carbon	QF	TOA	10	90 - 110	0.20 µg -C/m ³
Mass	TF	Gravimetric	± 10 µg	± 3 µg	2.13 µg /m ³
Trace/Crustal Elements	TF	XRF	20	90 - 110	0.001-0.10 ng/m ³

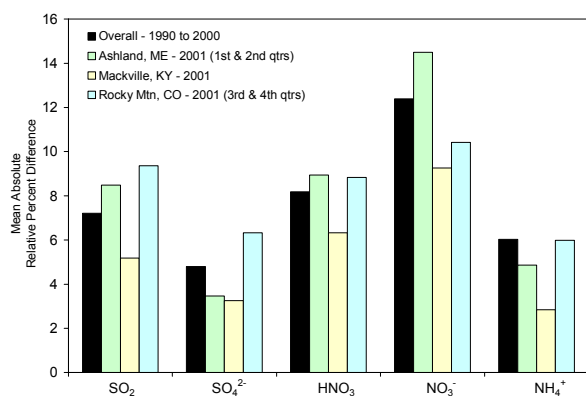
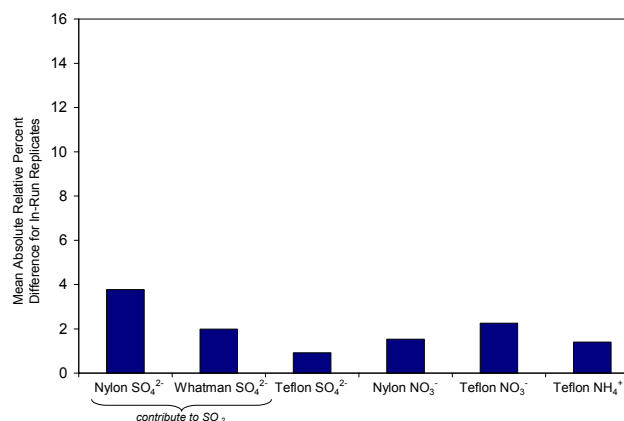
Note:

C = carbon
 F = filter pack samples
 ICAP-AE = inductively coupled argon plasma-atomic emission
 MARPD = mean absolute relative percent difference
 N = nitrogen
 QF = quartz filter samples
 TF = Teflo[®] filter samples
 TOA = thermal-optical analysis
 XRF = X-ray fluorescence

* The precision criteria apply to the laboratory analysis of field samples and laboratory replicates.

** This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples.

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNet Quality Assurance Project Plan (Harding ESE, 2002c).

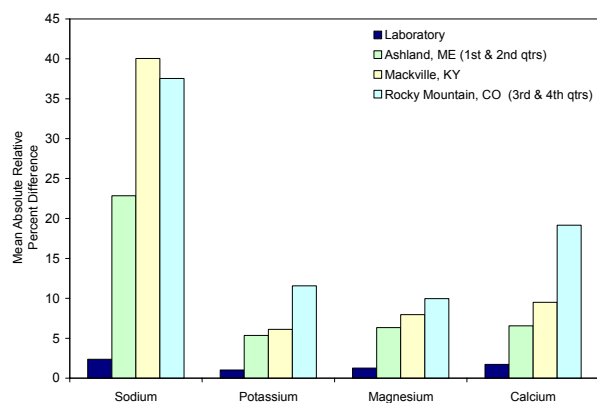
Figure 6-1. Historical and 2001 Precision Data for Atmospheric Concentrations**Figure 6-2.** Laboratory Precision Data for 2001

Note: The SO₄²⁻ analyzed on the Whatman and nylon filters constitutes ambient SO₂; the nylon NO₃⁻ provides ambient HNO₃; and the Teflon[®] SO₄²⁻ and NO₃⁻ provide ambient SO₄²⁻ and NO₃⁻, respectively.

The precision statistics for collocated Na^+ measurements were well above the 10 percent goal for all three sites. The MARPD for Na^+ measurements taken at ASH135/235 during 2001 was approximately the same as for 2000. The MARPD for Mackville more than doubled – from 17 percent to 40 percent. Harding ESE is investigating the results for Na^+ and will report any findings in quarterly reports during 2002. Chloride in the form of sodium chloride (NaCl) and potassium chloride (KCl) exists on blank Teflon[®] filters. Perhaps this is the source of the large Na^+ variability.

The 2001 precision statistics for the laboratory in-run replicate results for all cations for all sites met the criterion.

Figure 6-3. Precision Data for Cation Concentrations for 2001

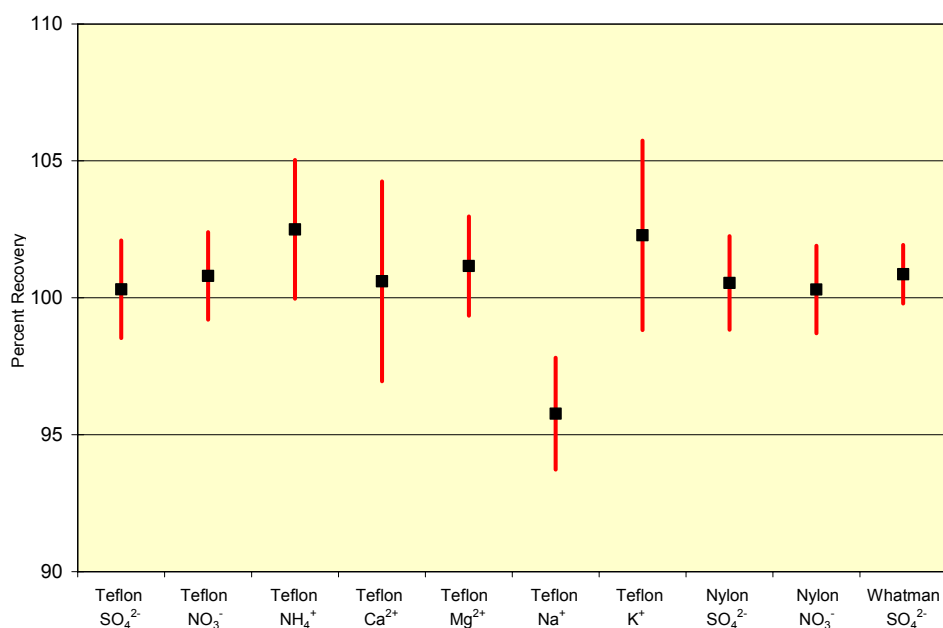


The precision of trace cation measurements was estimated from collocated samples collected at three sites in 2001. Precision estimates for K^+ , Mg^{2+} , and Ca^{2+} were acceptable for two of the three collocated sites. Precision of Na^+ measurements was unacceptable for all three sites.

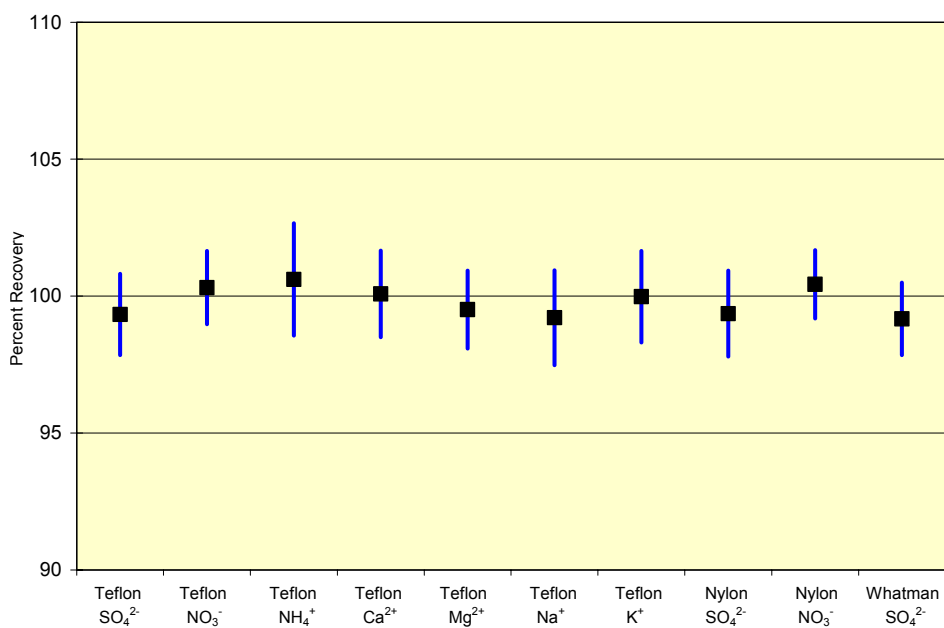
Accuracy of Laboratory Filter Concentrations

Accuracy of laboratory measurements is assessed through the analysis of reference samples and continuing verification samples (CVS). Reference samples, which are traceable to the National Institute of Standards and Technology (NIST), are procured from an independent laboratory supplier to simulate typical concentrations found on the dry deposition filters. NIST traceable inductively coupled argon plasma – atomic emission (ICAP-AE) reference samples are procured from the supplier of ICAP-AE calibration standards. The reference samples are produced separately from the calibration standards and have a different lot number. Reference samples are analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. The criteria are five percent for anions and 10 percent for cations (Table 6-1). Figure 6-4 presents the percent recovery relative to the certified reference values and its standard deviation for 2001. The criteria for reference sample accuracy were met in 2001 for all analytes and all filter types.

Accuracy is also assessed through the analysis of CVS. The CVS are NIST traceable. The target value of the CVS solution is set to the midrange of the calibration curve. The CVS in 2001 were analyzed every tenth sample to verify no drift in the calibration curve. Figure 6-5 presents the percent recovery of the CVS relative to the target concentrations. The standard deviation of each of the recovery values is also plotted. Because analysis of CVS is intended to prevent drift, a de facto goal for the standard deviation is ± 5 percent. During 2001, the DQI goals for CVS accuracy were met for all analytes and all filter types.

Figure 6-4. Reference Sample Recovery (percent) for 2001

Note: The square represents the sample recovery and the spread around each square represents its standard deviation.

Figure 6-5. Continuing Verification Sample Recovery (percent) for 2001

Note: The square represents the sample recovery and the spread around each square represents its standard deviation.

Table 6-2. Data Quality Indicators for CASTNet Field Measurements

Measurement Parameter	Method	Criteria*	
		Precision	Accuracy
Wind Speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or $\pm 5\%$ for winds ≥ 5 m/s
Wind Direction	Wind Vane	$\pm 5^\circ$	$\pm 5^\circ$
Sigma Theta	Wind Vane	Undefined	Undefined
Relative Humidity	Thin Film Capacitor	$\pm 10\%$ (of full scale)	$\pm 5\%$, rel. hum. $> 85\%$ $\pm 20\%$, rel. hum. $\leq 85\%$
Solar Radiation	Pyranometer	$\pm 10\%$ (of reading taken at local noon)	$\pm 10\%$
Precipitation	Tipping Bucket Rain Gauge	$\pm 10\%$ (of reading)	± 0.05 inch [†]
Ambient Temperature	Platinum RTD	$\pm 1.0^\circ\text{C}$	$\pm 0.5^\circ\text{C}$
Delta Temperature	Platinum RTD	$\pm 0.5^\circ\text{C}$	$\pm 0.5^\circ\text{C}$
Surface Wetness	Conductivity Bridge	Undefined	Undefined
O ₃	UV Absorbance	$\pm 10\%$ (of reading)	$\pm 10\%$
Filter Pack Flow	Mass Flow Controller	$\pm 10\%$	$\pm 5\%$
Light Scattering	Nephelometer	$\pm 15\%$	Undefined [§]

Note:

$^\circ\text{C}$	=	degrees Celsius
m/s	=	meters per second
rel. hum.	=	relative humidity
RTD	=	resistance-temperature device
UV	=	ultraviolet

* Precision criteria apply to collocated instruments and accuracy criteria apply to calibration of instruments.

[†] For target value of 0.50 inch.

[§] Nephelometer is replaced annually with a laboratory certified instrument

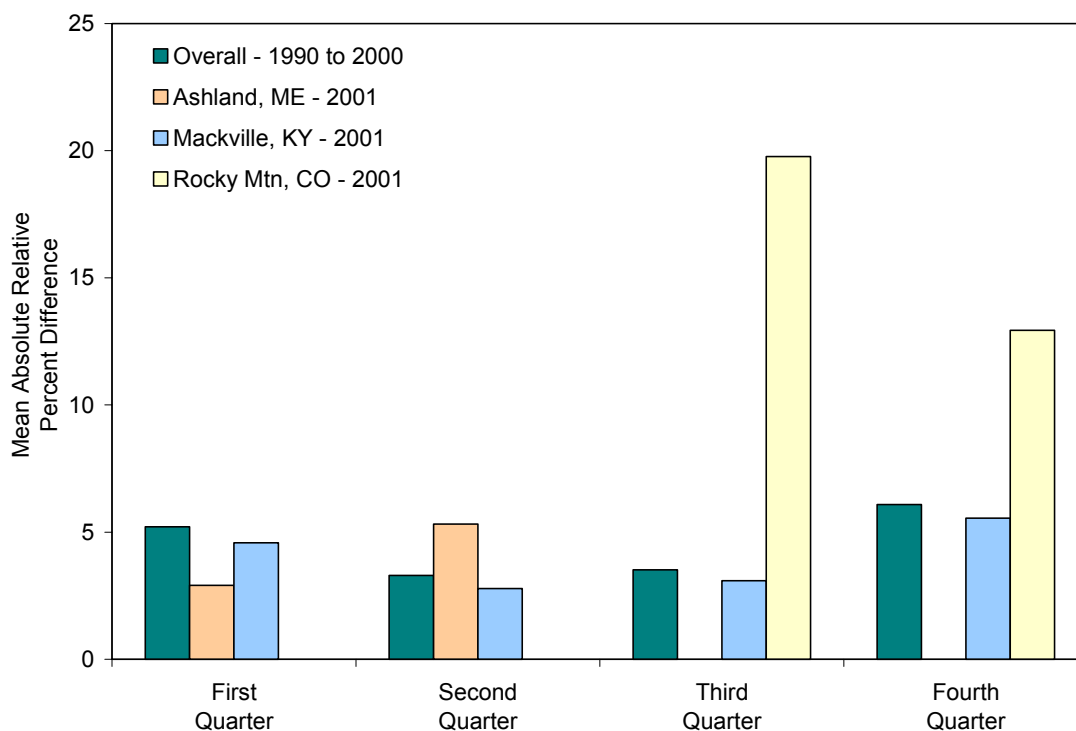
Precision of Ozone Concentrations

CASTNet QA procedures for the EPA O₃ analyzers are different from the EPA requirements for SLAMS monitoring as described in 40 CFR Part 68, Appendix A (EPA, 1998). On the other hand, the QA procedures for the O₃ analyzers at NPS sites meet the SLAMS requirements. The operation of the collocated O₃ analyzers at the Rocky Mountain National Park site provides an opportunity to evaluate the precision of the independent systems utilizing different QA/QC procedures.

Table 6-2 provides the DQI and associated measurement criteria for the CASTNet continuous measurements. The precision criterion for O₃ is 10 percent. MARPD statistics were calculated from hourly measurements obtained from the ROM206 and ROM406 O₃ analyzers that were operated during the third and fourth quarters of 2001. Precision data were also calculated from the O₃ measurements at ASH135/235 and MCK131/231. In addition, quarterly historical precision statistics (1990 through 2000) were compiled for all collocated sites. Quarterly precision results are shown in Figure 6-6.

Historical precision data for O₃ measurements were based on collocated samples from ten sites. The historical precision results met the 10 percent DQI goal. Results for 2001 for Ashland, ME and Mackville, KY were consistent with the historical data and achieved the goal. The precision data for the collocated analyzers at Rocky Mountain National Park, CO did not achieve the goal during 2001 because of instrument problems. However, results for the first quarter of 2002 indicated a 3 percent precision, well within the goal.

Figure 6-6. Historical and 2001 Precision Data by Quarter for Ozone Concentrations



The historical precision data show that the MARPD for the second and third quarters, the periods with the highest measured O₃ concentrations, were less than 5 percent. MARPD for the first and fourth quarters were approximately 5 to 6 percent. Results for 2001 for ASH135/235 and MCK131/231 were consistent with the historical data and achieved the DQI goal for O₃.

Unfortunately, the MARPD data for the collocated O₃ analyzers at ROM206/406 did not achieve the 10 percent criterion. The MARPD was about 20 percent for the third quarter and 13 percent for the fourth quarter. Failure to meet the criterion was not a result of different QA/QC procedures, but of

instrument problems that plagued the two O₃ systems during these two quarters. The NPS (ROM406) system's sample train leaked during most of July and from mid-August through the end of September. During the fourth quarter, the EPA's (ROM206) sample pump failed on October 6, 2001 and then operated only intermittently until November 21, 2001. The sample tower fell on December 11, 2001 and was repaired on January 3, 2002. Consequently, O₃ data comparability was poor during the second half of 2001. During the first quarter of 2002, both systems operated successfully and the quarterly MARPD value was approximately 3 percent (Harding ESE, 2002b).

The accuracy of the O₃ and other continuous measurements will be discussed in the CASTNet 2001 QA Report.

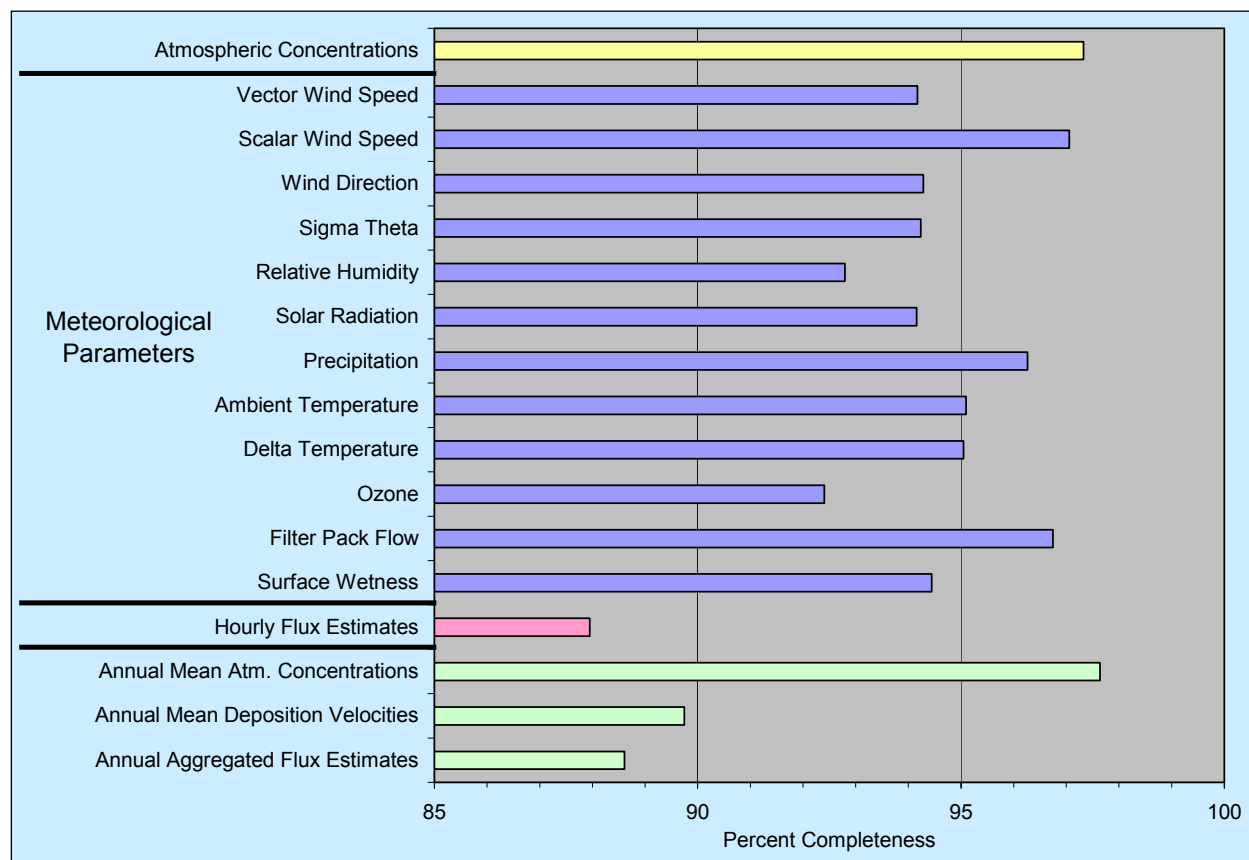
Completeness

Completeness is defined as the percentage of valid data points relative to total possible data points. The CASTNet DQI requires a minimum completeness of 90 percent for every measurement for each quarter. In addition, the data aggregation procedures discussed in Section D of the CASTNet QAPP (Harding ESE, 2002c) require approximately 70 percent data completeness for hourly fluxes and weekly concentrations/fluxes in order to calculate weekly and quarterly values, respectively.

Figure 6-6 presents 2001 completeness data aggregated over all sites for measured filter pack (dry deposition) concentrations and continuous measurements. In addition, completeness information for 2001 is presented for the calculated parameters: hourly dry deposition (flux) values, annual mean concentrations, annual mean deposition velocities, and annual flux estimates. The figure shows that direct measurements met the 90 percent goal. Filter concentrations and flow

values exceeded 95 percent; ozone data completeness was approximately 92.5 percent. The pink bar in Figure 6-6 depicts the completeness of hourly dry deposition fluxes. The fluxes were calculated from modeled V_d and measured concentrations. The modeled V_d depend on several measured meteorological variables, i.e., one missing meteorological parameter or leaf area index (LAI) value invalidates a V_d value. In other words, the completeness of the flux data depends on the combined completeness results for several parameters. The flux completeness was above 85 percent, which meets the criterion for flux completeness. The completeness of the annual mean concentrations, deposition velocities, and flux estimates all exceeded 85 percent.

For 2001, measured filter concentrations and continuous measurements exceeded 90 percent completeness. Hourly flux values, annual mean concentrations, annual mean deposition velocities, and annual flux estimates exceeded 85 percent completeness.

Figure 6-7. Percent Completeness of Measurements and Modeled Estimates for 2001

Summary

An analysis of DQI goals based on 2001 measurements and a review of historical results indicate that CASTNet has produced and continues to produce data of the highest quality. Estimates of field precision of collocated filter concentrations are reasonable given the complexity of the field, laboratory, and related measurement processes that contribute to measurement uncertainty. Historically, the precision statistics for SO_4^{2-} and NH_4^+ have met the DQI measurement criteria. The results for SO_2 and HNO_3 have been above the 5 percent criterion, but are considered reasonable. The precision data for NO_3^- have been significantly above the five percent goal. NO_3^- measurements have the largest

uncertainty. The results for 2001 are consistent with the historical results.

The 2001 results for analytical precision and accuracy met the DQI measurement criteria. The laboratory precision and accuracy data suggest that the analytical laboratory measurement processes represent only a small component of measurement uncertainty.

Historical O_3 precision data were well within the 10 percent criterion. MARPD estimates for ASH135/235 and MCK131/231 were consistent with historical results and met the criterion in 2001. Because of sampling problems with both the NPS and EPA sampling systems at ROM206/406, the O_3 measurements did not achieve the DQI goal during

the third and fourth quarters of 2001. Analysis of data collected in the first quarter of 2002 indicated that the systems were operating properly and estimated MARPD was about 3 percent.

CASTNet direct measurements met the completeness goal of 90 percent. Completeness

results for the calculated hourly fluxes, annual mean concentrations, annual mean deposition velocities, and annual fluxes were above 85 percent. These results are considered quite reasonable since they depend on the combined completeness of several measurements.